Proceedings of the ASME 2011 9th International Conference on Nanochannels, Microchannels, and Minichannels
ICNMM2011
June 19-22, 2011, Edmonton, Alberta, CANADA

ICNMM2011-58132

Deviation of the Calculated of Density of Refrigerant Fluids in Both Super and Sub Critical Regions

Neda Mobinipouya

Shiraz Islamic Azad University
Shiraz, Iran
E-mail: mobinipouya@*yahoo.com*

Abstract

A numerical procedure has successfully predicted accurate values of thermodynamic properties in seven cubic equations of state (EOS) in predicting thermodynamic properties of nine ozone-safe refrigerants both in super and sub-critical regions. Refrigerants include R22, R32, R123, R124, R125, R134a, R141b, R143, and R152a and equations of state, considered here, are Ihm-Song-Mason (ISM), Peng-Robinson (PR) [2] , Redlich-Kwong (RK), Soave-Redlikh-Kwong (SRK) , Modified Redlickh-Kwong (MRK), Nasrifar-Moshfeghian (NM), and TCC were shown in this paper.

In general, the results are in favor of the preference of TCC and PR EOS over other remaining EOS's in predicting gas densities of all aforementioned refrigerants in both super and sub critical regions. Typically, PR and SRK are in good agreement with those obtained from recent correlations and speed of sound measurements. Therefore, these two EOS stand over other EOS both in sub and super critical regions . All EOS follow two-parameter principle of corresponding states at T/Tc higher than 8 and lower than 1 except NM EOS. In the temperature range 1<T/Tc<8, PR and SRK still follow above mentioned principle. The same trend has been observed for other refrigerants.

***Keywords*—**Refrigerant;Redlich-Kwong;Sub-Critical Regions Super Critical Regions

INTRODUCTION

Since van der Waals (1873) proposed his well-known cubic equation of state over a century ago, numerous equations of state have been proposed to calculate the thermodynamic properties of both pure components and mixtures in vapor and liquid phases.

The ability of a CEOS to correlate the phase equilibria of mixtures depends not only on the mixing rule, but also on the alpha function. Remarkable success in the development of a generalized alpha function was shown by Soave (1972) He recognized that a prerequisite for the correlation of the phase equilibria of mixtures is the correlation of the vapor pressures of the pure components.The soave modification of the Redlich and Kwonog(1949) equation has been a major success in correlation of the phase behavior of multi-component systems containing non-polar and slightly polar components. The soave approach was subsequently used in work by peng and Robinson (1976) [2]. This also helped the PR equation to become one of the most widely used equations of state in industry for correlating the vapor – liquid equilibria (VLE) of systems containing non-polar and slightly polar components.

History

Equations of state play an important role in chemical engineering design and they have assumed an expanding role in the study of the phase equilibria of fluids and fluid mixtures.Originally, equations of state were used mainly for pure components. When first applied to mixtures, they were used only for mixtures of nonpolar (Soave, 1972; Peng and Robinson[2] , 1976) and slightly polar compounds (Huron et al., 1978; Asselineau et al., 1978; Graboski and Daubert, 1978). Since then, equations of state have developed rapidly for the calculation of phase equilibria in non-polar and polar mixtures. The advantage of the equations of state method is its applicability over wide ranges of temperature and pressure to mixtures of diverse components, from the light gases to heavy liquids. They can be used for the representation of vapour-liquid, liquid-liquid and supercritical fluid phase equilibria and they can be also applied to the gas, liquid and supercritical phases without encountering any conceptual difficulties.Many equations of state have been proposed in the literature with either an empirical,semi-empirical or theoretical basis. Comprehensive reviews can be found in the works of Martin (1979), Gubbins (1983), Tsonopoulos and Heidman (1985) [9], Han et al. (1988), Anderko (1990), Sandler (1994) and Donohue and Economou (1995).

REVIEW OF EQUATIOINS OFSTATE

Van der Waals EOS

$$(P + \frac{a}{V_m{}^2})(V_m - b) = RT$$

(1)

Where p represents pressure, T is temperature, V_m is molar volume and R is the molar gas constant.The parameter a is a measure of the attractive forces between the molecules and the parameter b is a measure of the size of the molecules (hard body term). Both adjustable parameters a and b can be obtained from the critical properties of the fluid. The van der Waals equation can be regarded as a "hard-sphere (repulsive) + attractive" term equation of state composed from the contribution of repulsive and attractive intermolecular interactions, respectively.

It gives a qualitative description of the vapour and liquid phases and phase transitions (Van Konynenburg and Scott, 1980), but it is rarely sufficiently accurate for critical properties and phase equilibria calculations. A simple example is that for all fluids, the critical compressibility predicted by Eq.(1.1) is 0.375, whereas the real value for different hydrocarbons varies from 0.24 to 0.29. The van der Waals equation has been superseded by a large number of other, more accurate equations of state.

Where a, b and R are constants that depend on the specific material.

Proposed in 1873, the van der Waals equation of state was one of the first to perform markedly better than the ideal gas law. In this landmark equation a is called the attraction parameter and b the repulsion parameter or the effective molecular volume. While the equation is definitely superior to the ideal gas law and does predict the formation of a liquid phase, the agreement with experimental data is limited for conditions where the liquid forms. While the van der Waals equation is commonly referenced in text-books and papers for historical reasons, it is now obsolete. Other modern equations of only slightly greater complexity are much more accurate. Van der Waals equation may be considered as the ideal gas law, "improved" due to two independent reasons:

1.Molecules are thought as particles with volume, not material points. Thus V cannot be too little, less than some constant. So we get (V - b) instead of V.

2. While ideal gas molecules do not interact, we consider molecules attracting others within a distance of several molecules' radii. It makes no effect inside material, but surface molecules attract to inside. We see this as diminishing of pressure on the outer shell (which is used in the ideal gas law), so we write (P + something) instead of P. To evaluate this 'something', let's examine addition force acting on an element of gas surface.

R edlich-Kwong EOS

Introduced in 1949 the Redlich-Kwong[4] equation of state was a considerable improvement over other equations of the time. It is still of interest primarily due to its relatively simple form. While superior to the van der Waals equation of state, it performs poorly with respect to the liquid phase and thus cannot be used for accurately calculating vapor-liquid equilibria. However, it can be used in conjunction with separate liquid-phase correlations for this purpose.. The Redlich-Kwong equation is adequate for calculation of gas phase properties when the ratio of the pressure to the critical pressure (reduced pressure) is less than about one-half of the ratio of the temperature to the critical temperature (reduced temperature).The Redlich-Kwong EOS by Redlich and Kwong is a modification of the Van der Waals EOS it should only be used in order to demonstrate the inabilities of simple EOS ,because better EOS exist . Use of this EOS only requires the input of Tc and Pc.

The parameters a and b (for each component):

$$p = \frac{RT}{v-b} - \frac{\alpha}{\sqrt{T}v(v+b)} \qquad (2)$$

$$a = 0.42748 \frac{R^2 T_C^{2.5}}{P_c} \qquad (3)$$

$$b = \frac{0.0778\, RT_c}{P_c} \qquad (4)$$

R = ideal gas constant (8.31451 J/ (mol·K))

Peng-Robinson EOS [2]

This equation of state is fairly similar to the Soave-Redlich-Kwong equation ,but with a slightly different denominator for the second term.Again , the parameter has a temperature dependence, and the parameter giving its dependence have been found by comparing the predictions of the equation with experimental boiling points.The Peng-Robinson equation[2] is particularly accurate for predicting the properties of ydrocarbons, including the behavior of mixtures and vapor-liquid equilibrium. It is not expected to be accurate when predicting properties properties of highly polar molecules, particularly those that are capable of hydrogen bonding.The Peng-Robinson EOS[2] is the EOS most widely used in chemical engineering thermodynamics.The EOS requires three inputs per compound: Tc, Pc and the acentric factor w.

The Peng-Robinson EOS[2] is the EOS most widely used in chemical engineering thermodynamics.The EOS requires three inputs per compound: Tc, Pc and the acentric factor ω.

ISM EOS

This EOS was derived by Song and Mason from statistical-mechanical perturbation theory. We confine ourselves to offer it here briefly because the detail of the derivation has been given elsewhere. The aforesaid EOS is of the following from:

$$\frac{P}{\rho kT} = 1 + \frac{(B_2 - \alpha)\rho}{1 + \delta b\rho} + \frac{\alpha\rho}{1 - \lambda b\rho} \qquad (5)$$

δ is proportional to λ such that δ = 0.22λ.Because the theoretical foundation of this EOS involves a mean field approximation, it can be applied to predict the PVT data at any pressure and temperature, except the critical and two – phase regions.If the values of B2, a, and b are known, the free parameter λ will be determined experimentally form high-density PVT data such as liquid density.The major problem now is to find parameters B2 , a , and b .These

parameters have been obtained from speed of sound data using a macroscopic corresponding states correlation .

Nasrifar-Moshfeghian EOS[6]

A two-parameter cubic equation of state is developed. Both parameters are taken temperature dependent. Methods are also suggested to calculate the attraction parameter and the co-volume parameter of this new equation of state.For calculating the thermodynamic properties of a pure compound, this equation of state requires the critical temperature, the critical pressure and the Pitzer's acentric factor of the component.

$$P = \frac{RT}{v-b} - \frac{a}{v^2 + 2bv - 2b^2} \qquad (6)$$

$$a = a_c[1 + m_a(1-\sqrt{\theta})]^2 \qquad (7)$$

$$b = \frac{0.0778\ RT_c}{P_c} \qquad (8)$$

$$\theta = \frac{T - T_{PT}}{T_C - T_{pt}} \qquad (9)$$

TCC EOS

The new equation of state has the same form as that proposed by Peng and Robinson[2] (1976),but with different generlized alpha function .The subscript c denotes the critical point, b is kept constant and a is function of temperature .

$$P = \frac{RT}{V-b} - \frac{a\alpha}{(V^2 + \delta V + \varepsilon)} \qquad (10)$$

Calculation of Second virial coefficient

A close look at figures reveals that PR and SRK are in good agreement with those obtained from recent correlations obtained by Tsonopoulos[9] and Weber[10] and speed of sound measurements.Therefore, these two EOS stand over other EOS both in sub and super critical regions.All EOS follow two-parameter principle of corresponding states at T/Tc higher than 8 and lower than 1 except NM EOS.In the temperature range 1<T/Tc<8, PR and SRK still follow above mentioned principle.The same trend has been observed for other refrigerants

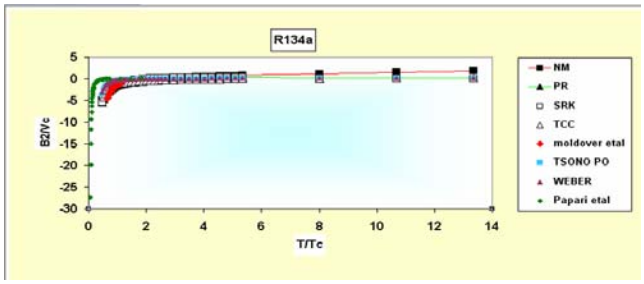

Figure 7: As a thermodynamic property, second virial coefficients of R143a have been calculated from NM EOS., PR EOS. , SRK EOS. TCC EOS.

Conclusion

In sum the results are in favor of the preference of TCC and PR EOS's over other remaining EOS's in predicting vapor densities of all mentioned refrigerants in both super and sub critical regions.

References:

[1]Y. Song, E. A. Mason, *J. Chem. Phys*. 91, 7840 (1989).
[2]D. Y. Peng, and D. B. Robinson, *Ind. Eng. Chem. Fundam*. 15, 59 (1976).
[3]O. Redlich and J. N. S. Kwong, *Chem. Rev*. 44, 233 (1949).
[4]G. Soave, *Chem. Eng. Sci*. 27, 1197 (1972).
[5]G. Soave, *Fluid Phase Equilib.* 82, 345 (1993).
[6]Kh. Nasrifar, M. Moshfeghian, *Fluid Phase Equilibria* 190, 3 (2001).
[7]C. H. Twu, J. E. Coon, J. R. Cunningham, *Fluid Phase Equilib*., 105, 49 (1995).
[8]S. Sheikh, M. M. Papari, A. Boushehri, Ind. Eng. Chem. Res., 41 (2002) 3274
[9]C. Tsonopoulos, Fluid Phase Equilibria, 21, 35 (2003)
[10]L. A. Weber, Int. J. Thermophys, 15, 461 (1994)